# STUDY OF THERMAL PROPERTIES OF REFRACTORIES
## (SECOND QUARTERLY PROGRESS REPORT)

R. E. Taylor
M. M. Nakata

Contract No. AF 33(657)-7136
ARPA Order No. 24-61
Project No. 002

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January 1962



ATOMICS INTERNATIONAL
A Division of North American Aviation, Inc.
Canoga Park, California

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## FOREWORD

The work reported here was performed by Atomics International, a Division of North American Aviation, under the auspices of the Department of Defense through the Advanced Research Project Agency. Contract AF 33(657)-7136 issued under ARPA Order No. 24-61, Project 002, "Materials Thermal Properties" was administered by the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. Hyman Marcus acting as project engineer. This report covers work conducted from October 1, 1961 to December 31, 1961

This investigation is an extension of work previously performed under Contract AF 33(616)-6794. The present work is under Dr. S. C. Carniglia of the Fuels and Materials Department.

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## ABSTRACT

A status report is presented on the development of the transient thermal property apparatus described in Parts I and II of WADD-TR-60-581. Refinements of the apparatus are described and results of measurements are given for the thermal diffusivity of tantalum from 1300° to 1650°C and for the diffusivity of zirconium carbide from 1300° to 1600°C. The status of thermal property measurements by existing techniques is included. Results of thermal conductivity measurements of zirconium carbide from 450° to 1820°C and of the specific heat of titanium carbide from 100° to 730°C are shown.

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# STUDY OF THERMAL PROPERTIES OF REFRACTORIES

by R. E. Taylor and M. M. Nakata

## I. INTRODUCTION

The primary purpose of this project is to measure, describe, and understand the thermal properties of refractory materials from ambient temperature to temperatures approaching the melting point. This quarterly progress report covers the period from October 1, 1961 to December 31, 1961.

Minor modifications of the apparatus for transient thermal property measurements have been made, based on the operating experience accumulated to date. Greater ease in the critical alignment of samples was achieved. Measurements on tantalum were extended to encompass the range 1300° to 1650°C. Results have, with few exceptions, been within a maximum deviation of 7% from literature values and have been typically within 4%. Measurements on "as-received" and "heat-treated" zirconium carbide were made from 1300° to 1600°C. This phase of the work is described in Section II.

In order to obtain information on the thermal properties of refractory materials during the development of new approaches and to provide information for intercomparing results, an effort utilizing existing techniques has been maintained. Previously obtained results on the thermal conductivity of titanium carbide were verified off-site. Thermal conductivity results on three specimens of zirconium carbide are reported from 450° to 1820°C. This work is described in Section III.

The specific heat of one sample of titanium carbide was measured from 150° to 750°C by the pulse heating technique. The results are described in Section IV.

## II. STATUS REPORT ON TRANSIENT THERMAL PROPERTY APPARATUS

The transient thermal diffusivity apparatus has been performing satisfactorily up to approximately 1650°C. Since the last report, additional measurements were obtained for tantalum in the temperature range 1300° to 1650°C, and also for zirconium carbide in the range 1300° to 1600°C.

The reproducibility of the photoelectric pyrometer output has been brought up to a high level with very little background noise. A positioning device (an adaptation of a microscope stage) was also incorporated to facilitate the alignment of the collimator with the sample and pyrometer. The technique for aligning the sample, shieldings, collimator, and pyrometer has been improved. The only difficulty experienced with the present setup is in the design of the upper radiation shields. At temperatures above 1600°C, especially after several thermal cyclings, there is a tendency for the tantalum shields to shift out of place due to thermal expansion. The ceramic sight tubes are then also forced out of alignment with the sample holes. This is indicated immediately on the chart as an abrupt change in the photocurrent.

A new shielding designed to prevent this difficulty has been designed, and the fabrication of the parts is under progress. In the meantime, measurements up to 1600° and possibly to 1700°C can be continued using the existing shieldings.

Table I shows the thermal diffusivity values obtained for two samples of tantalum. The first 6 runs are for sample Ta-A-1; runs 7 through 14 are for sample Ta-B-1. The data are also shown in Figure 1.

TABLE I

Thermal Diffusivity of Tantalum

$a$ $cm^2/sec$

| Run No. | 1300°C | 1400°C | 1500°C | 1600°C | 1650°C |
|---|---|---|---|---|---|
| 1 | | .215 | .215 | | |
| 2 | | .228 | .203 | | |
| 3 | | .215 | .203 | | |
| 4 | | .209 | .215 | | |
| 5 | | .222 | .224 | | |
| 6 | | .210 | .252 | | |
| 7 | | .240 | .236 | | |
| 8 | | .215 | .225 | | |
| 9 | | .216 | .232 | | |
| 10 | .212 | .215 | .224 | .217 | .237 |
| 11 | | .195 | .227 | .260 | .225 |
| 12 | .202 | .211 | .237 | | |
| 13 | | .205 | .239 | | |
| 14 | | .192 | .214 | | |

The short solid horizontal lines in the Figure represent the mean at each of the temperatures. The standard deviations at 1400° and 1500°C are 0.012 and 0.013 $cm^2/sec$, respectively. For comparison, the diffusivity values calculated from specific heat[1] and thermal conductivity[2] data previously obtained at this laboratory are shown by means of the broken line. As one can see, the agreement between the transient data and the calculated data is very good.

The apparent scarcity of data at 1300°C is not due to experimental difficulty, but simply because more data at the higher temperatures were sought.

A closer check on the reliability of the data can be made if the shifting of the pyrometer between the sight holes is kept to

not more than two cycles per chart span, simply because any small fluctuation in the photocurrent output due to zero shifting or misalignment can be detected with more certainty. In other words, too many cycles will have the tendency of masking the small fluctuations. Each run, therefore, gives data over a limited temperature interval of approximately 150°, but with better reliability.

The zirconium carbide test results are given in Table II, and are also shown in Figure 1. The zirconium carbide was obtained from the Carborundum Co., Niagara Falls, New York, and was fabricated by hot pressing techniques. Three diffusivity samples were machined out of the as-received compact. The sample reported here, ZrC-B-1, had a density of 6.24 $g/cm^3$ before the diffusivity runs.

TABLE II

Thermal Diffusivity of Zirconium Carbide

$\alpha$ $cm^2/sec$

| Run No. | 1300°C | 1400°C | 1500°C | 1600°C |
|---|---|---|---|---|
| 1 | | .123 | .124 | .123 |
| 2 | | .125 | .136 | |
| 3 | .126 | .128 | .129 | .142 |
| 4 | .113 | .117 | .126 | .138 |
| 5 | .121 | .126 | .138 | |
| 6 | .114 | .120 | .133 | |
| 7 | | .120 | .121 | |

The reproducibility of data was much better with zirconium carbide than with tantalum, which is understandable if one compares the diffusivities of the two materials. Since the experimental data consists of measuring the time interval $\Delta t$ in the equation[3]

$$\alpha = \frac{r_2^2 - r_1^2}{4\Delta t} ,$$

a larger diffusivity will mean a smaller $\Delta t$. The precision of measurements will therefore increase with decreasing diffusivity values.

The mean at each temperature is again indicated with short solid lines, and the calculated value at 1500°C is indicated with a short broken line. The value used for thermal conductivity was obtained from Section III of this report, and the value of specific heat was obtained from Southern Research Institute.[4] The standard deviations at 1400° and 1500°C are .004 and .006 $cm^2/sec$, respectively. It should be noted here that two preliminary runs gave diffusivity values of .080 and .092 $cm^2/sec$, but the source of this discrepency has not been determined. Additional measurements with different samples of zirconium carbide are contemplated with the aim of determining whether this anomaly is real or due to experimental fault.

Two titanium carbide samples have been procured, and machining of one of these samples has been completed so that test runs may be made in the near future.

## III. STATUS REPORT ON STEADY STATE THERMAL CONDUCTIVITY APPARATUS

The thermal conductivity of titanium carbide was previously measured and reported.[5] These results are in serious disagreement with the results of Vasilos and Kingery[6] who are the only other investigator of the high temperature thermal conductivity of this material. Therefore, samples of titanium carbide were sent to Dr. Michael Hoch of the University of Cincinnati who agreed to act as an independent observer. Dr. Hoch made two measurements of the ratio of the thermal conductivity to the total emissivity and obtained $\frac{k}{\epsilon} = 0.315$ and 0.291 at 966° and 1474°C, respectively. He assumed that the total emissivity of titanium carbide was identical to that of titanium metal (0.25 at 966° and 0.31 at 1474°C). Using these values for $\epsilon$, the thermal conductivity was calculated to be 0.079 cal/cm·°C·sec at 966° and 0.090 cal/cm °C sec at 1474°C. The total emissivity of titanium carbide is believed to be somewhat higher than that of the metal and, therefore, the above values are in good agreement, with respect to both magnitude and temperature coefficient, with the results obtained in this laboratory.

The thermal conductivity of three samples of zirconium carbide was measured from 450° to 1820°C in the steady state apparatus.[7] These results are given in Table III and plotted in Figure 2.

TABLE III

Thermal Conductivity of Zirconium Carbide

| Data Point | Thermal Conductivity, cal/cm·°C·sec | | | Temperature °C |
|---|---|---|---|---|
| | Sample 2 | Sample 3 | Sample 4 | |
| 1 | | 0.0787 | | 695 |
| 2 | | 0.0771 | | 783 |
| 3 | | 0.0798 | | 899 |
| 4 | 0.0785 | | | 607 |
| 5 | 0.0851 | | | 726 |
| 6 | 0.0773 | | | 803 |
| 7 | 0.0794 | | | 917 |
| 8 | 0.0782 | | | 851 |
| 9 | 0.0768 | | | 775 |
| 10 | | 0.0720 | | 548 |
| 11 | | 0.0840 | | 777 |
| 12 | 0.0815 | | | 698 |
| 13 | 0.0856 | | | 826 |
| 14 | 0.0749 | | | 547 |
| 15 | 0.0838 | | | 626 |
| 16 | 0.0851 | | | 728 |
| 17 | 0.0856 | | | 665 |
| 18 | 0.0822 | | | 741 |
| 19 | 0.0840 | | | 833 |
| 20 | 0.0868 | | | 944 |
| 21 | 0.0785 | | | 742 |
| 22 | | 0.0777 | | 888 |
| 23 | | 0.0832 | | 783 |
| 24 | | 0.0785 | | 718 |
| 25 | 0.101 | | | 1343 |
| 26 | 0.0950 | | | 1463 |
| 27 | 0.0968 | | | 1524 |
| 28 | 0.0909 | | | 1586 |
| 29 | 0.0885 | | | 1258 |
| 30 | 0.0925 | | | 1320 |
| 31 | | | 0.0989 | 1231 |
| 32 | | | 0.0932 | 1338 |
| 33 | | | 0.0917 | 1440 |
| 34 | | | 0.0922 | 1569 |
| 35 | | | 0.102 | 1368 |
| 36 | | | 0.0979 | 1435 |
| 37 | | | 0.0942 | 1500 |
| 38 | | | 0.101 | 1618 |
| 39 | | | 0.0927 | 1703 |
| 40 | | | 0.0976 | 1654 |
| 41 | | | 0.101 | 1825 |
| 42 | | | 0.086 | 1100 |
| 43 | 0.0850 | | | 1023 |

It can be seen in Figure 2 that the values obtained on the three specimens overlap, and all the data can be described within 10% by one curve. The thermal conductivity of zirconium carbide increases with increasing temperature in a manner similar to that previously observed for titanium carbide. In fact the curves are almost parallel from 450° to 1820°C with the conductivity of zirconium carbide displaced about 0.01 cal/cm·°C·sec below that of titanium carbide.

The only other high temperature thermal conductivity measurements on zirconium carbide were recently made at Southern Research Institute.[4] The present results are approximately 20% below their smoothed value at 500°C and 10% below their smoothed value at 1800°C. However, the scatter in the Southern Research Institute data, especially between data obtained on different specimens, was such as to encompass the present results. The smooth curves generated at Southern Research Institute and our laboratory are within the combined experimental error of 13% above 1000°C.

The zirconium carbide specimens used in the present work were hot pressed specimens obtained from the Carborundum Company. They are characterized in Table IV.

TABLE IV

ZrC Sample Histories

| | Sample No. 2 | Sample No. 3 | Sample No. 4 |
|---|---|---|---|
| Fabrication Method | Hot pressed | Hot pressed | Hot pressed |
| Fabrication Date | 1960 | 1957 | 1960 |
| Density $gm/cm^3$ | 6.13 | 6.17 | 6.18 |
| X-ray Results | Single phase | Single phase | Single phase |
| Microstructure | • | • | • |
| Chemical Analysis of Powder | | | |
| Wt. % Zr | 87.94 | •• | 87.94 |
| Wt. % C | 11.30 | •• | 11.30 |
| Wt. % Fe | 0.1 | •• | 0.1 |
| Wt. % Other Metals | 0.2 | •• | 0.2 |
| Chemical Analysis of Hot Pressed Material - As-Received | | | |
| Wt. % Zr | 87.6 | 87.85 | 87.6 |
| Wt. % C | • | 12.14 | • |
| Wt. % Fe | • | 0.39 | • |
| Wt. % Other Metals | • | 0.33 | • |
| At Conclusion of Measurements | | | |
| Wt. % Zr | ••• | ••• | ••• |
| Wt. % C | ••• | ••• | ••• |
| Wt. % Fe | ••• | ••• | ••• |
| Wt. % Other Metals | ••• | ••• | ••• |

• Under Investigation

•• Unknown

••• To be Determined

## IV. STATUS REPORT ON PULSE HEATING TECHNIQUE FOR SPECIFIC HEAT DETERMINATIONS

The electrical resistivity of a specimen of titanium carbide was previously measured from 25° to 780°C.[5] This specimen was pulse heated over the same temperature range and the specific heat determined. The results are shown in Figure 3. The results of Naylor,[8] the only other investigator of the specific heat of titanium carbide above room temperature, are also shown in Figure 3. The data agree within 5% above 550°C.

The major problem hindering efforts to measure specific heats to the melting temperature is the lack of accurate electrical resistivity data at high temperature. Developmental work on this apparatus is continuing.

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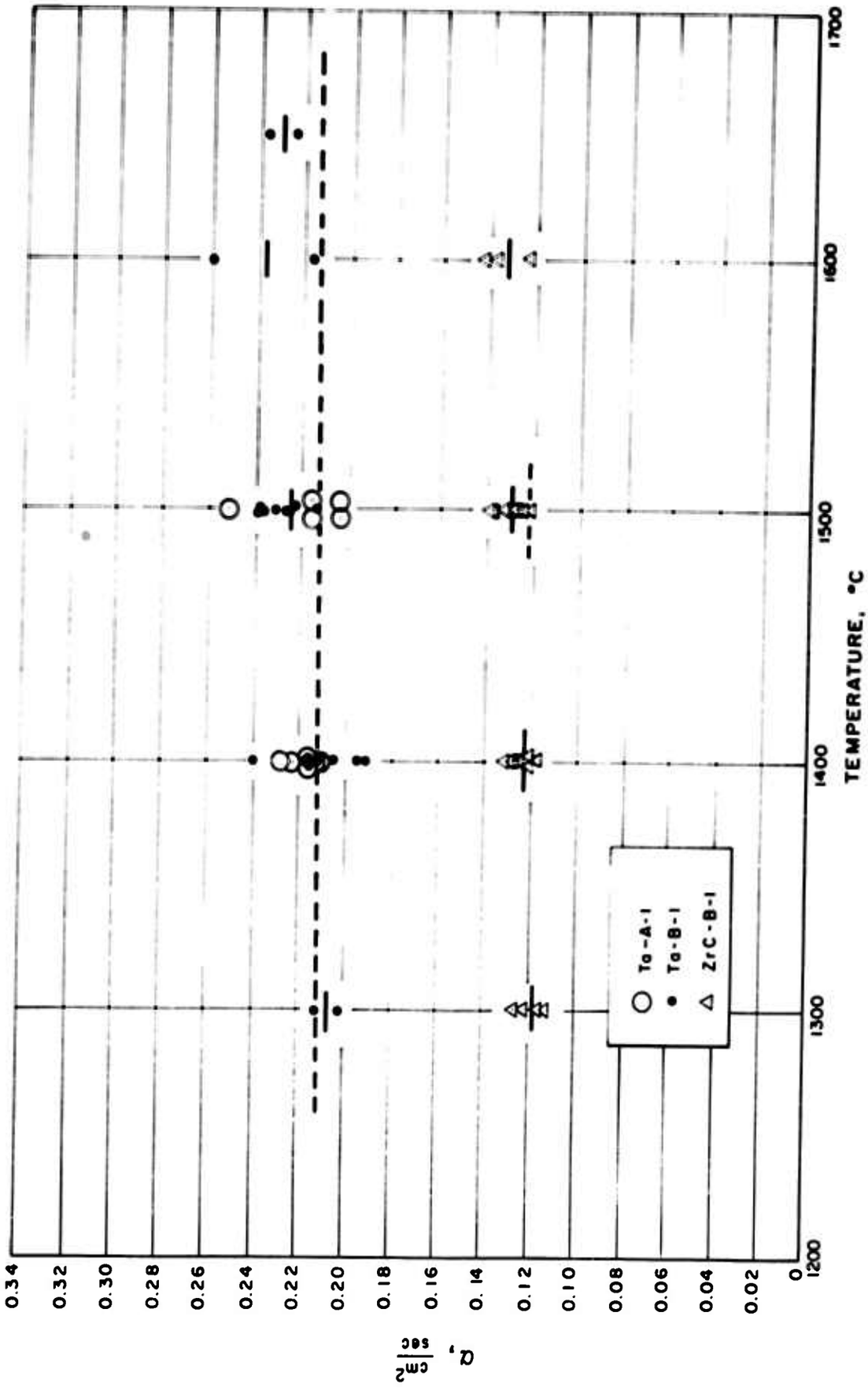


Figure 1 Thermal Diffusivity of Tantalum and Zirconium Carbide

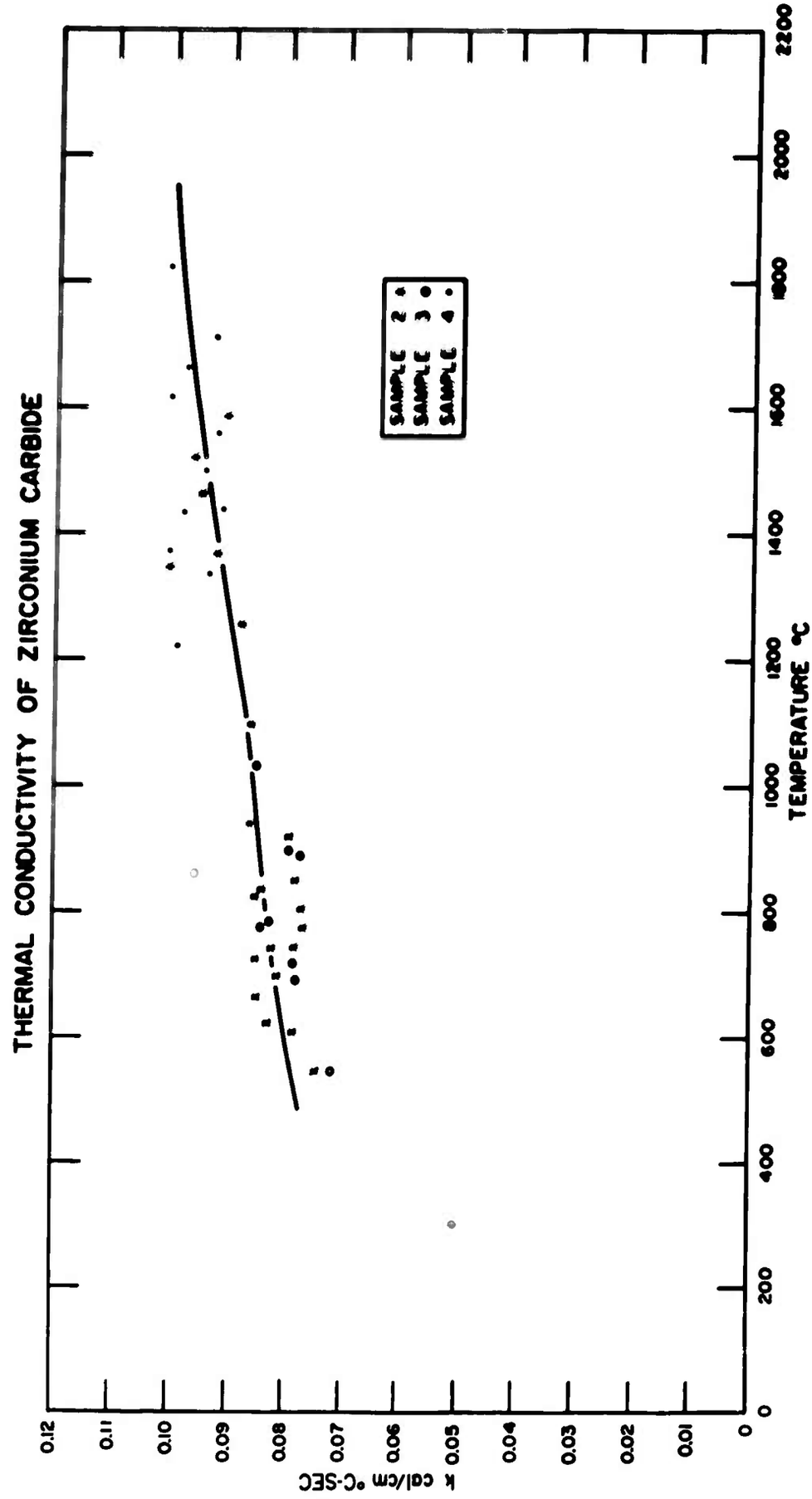
THERMAL CONDUCTIVITY OF ZIRCONIUM CARBIDE
SAMPLE 2 ▲
SAMPLE 3 ●
SAMPLE 4 ▪
k cal/cm °C-SEC
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
TEMPERATURE °C

Figure 2

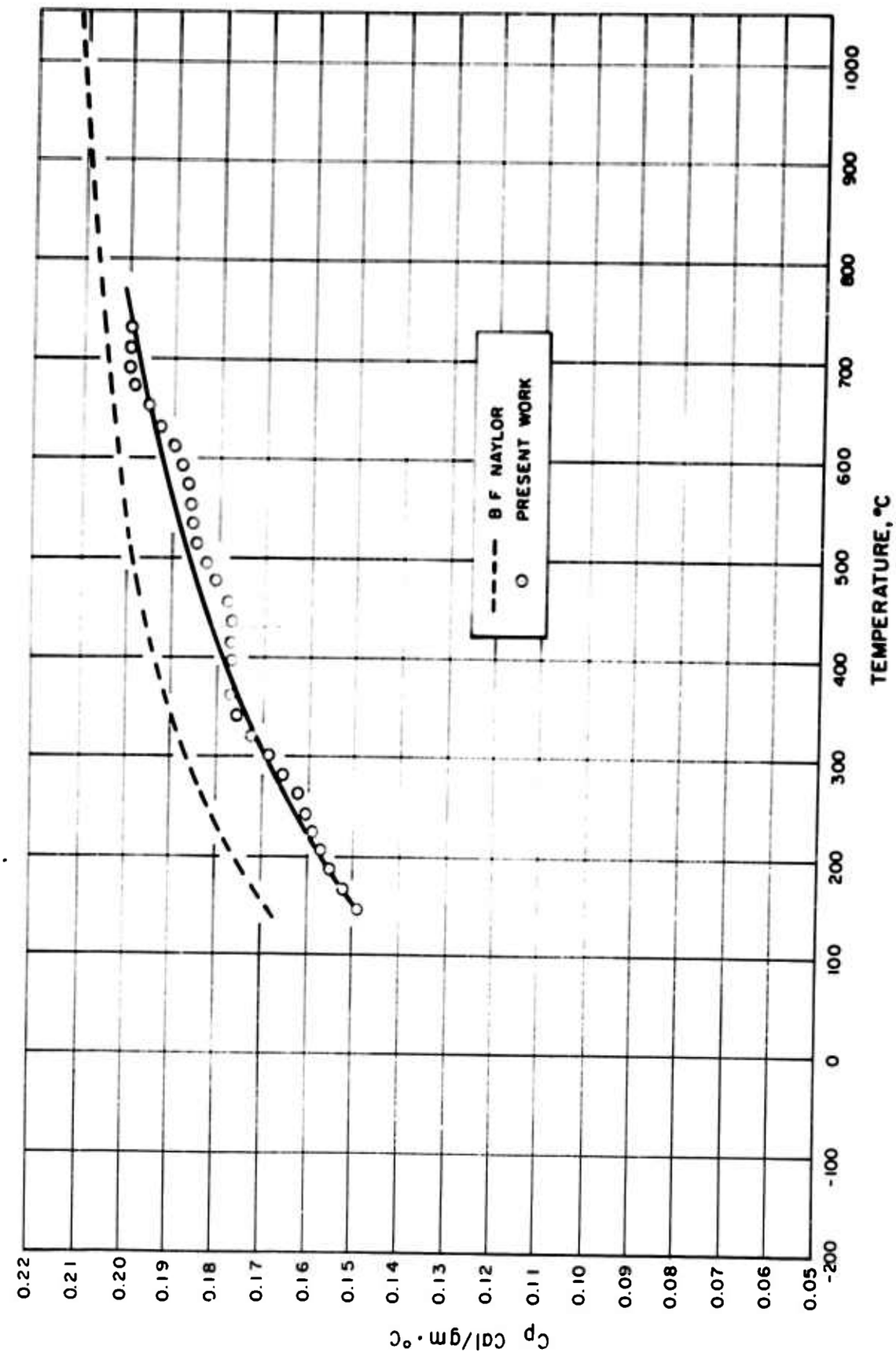


Figure 3 Specific Heat of Titanium Carbide

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